UNIVERSITY OF PENNSYLVANIA

A NEW PROCEDURE FOR THE DETERMINATION OF UNSATURATION OF ORGANIC COMPOUNDS BY BROMINATION, AND A STUDY OF SOME ERRORS WHICH AFFECT BROMINATION METHODS

HOWARD McWILLIAMS BUCKWALTER

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IN CHEMISTRY
PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. Introduction

Organic unsaturation of the olefinic type is usually determined analytically by halogen-absorption methods, such as the following:

Primary Method		Modifications	
Author	Active Agent	Author	Active Agent
Hübl[1]	ICl (iodine, $HgCl_2$ in alcohol)	Ingle[25]	I and $HgCl_2$ kept separate until used
Wijs[2]	ICl in glacial acetic acid	Marshall[24] Kemp[13]	ICl in CCl_4 ICl in glacial acetic acid
Hanûs[3]	IBr in glacial acetic acid	Marshall[24]	IBr in CCl_4
Klimont[29]	Br ($KBrO_3$ + KBr + acid) in water and $CHCl_3$	Crossley-Renouf[27] Francis[12]	Br_2 in $CHCl_3$; Br ($KBrO_3$ + KBr + acid) in water
McIlhiney[4]	Br in CCl_4	Schweitzer & Lungwitz[21]	Br in CCl_4

The usefulness of a halogen-absorption method for determination of unsaturation depends upon the extent to which it satisfies several criteria:

(1) Addition of halogen at multiple bonds must be quantitative.

(2) Substitution must be either
   (a) Negligible in methods which offer no facilities for determining the hydrogen halide of substitution, or
   (b) determinable with accuracy in methods which permit such an operation.

(3) Both addition and substitution must be irreversible or substantially so.

(4) Interference due to secondary action of reagents used to complete the analysis must be either absent or determinable.

In judging the comparative merits of the iodine-halide methods and the bromine methods, it is necessary to bear in mind that the tendency to substitution is nearly always present (4a,6), and probably varies more or less directly with the halogenating power of the reagent as measured by its ability to effect halogen-addition.

The iodine-halide methods, which in general involve a milder action, are probably in many cases not much affected by errors due to substitution (30), but such errors as enter cannot be evaluated, due to the nature of the reagent (except in Johansen's and Marshall's methods). Because of this same milder action, however, iodine-halide methods are in general less certain in the complete saturation of multiple bonds, especially those which for any reason are less accessible to halogenation (*e.g.,* alpha-unsaturated acids). Longer periods of contact with the reagent are then required, and in such cases, assuming saturation to be complete, the results may be affected by an indeterminable positive error due to substitution.

For the analysis of certain classes of unsaturated substances, such as fats and oils, certain of the iodine-halide methods have been found by experience to be useful, saturation occurring so quickly and substitution (if any) so slowly (35,36), that the results are satisfactory. The method of Wijs, now accepted as most useful (36) for analysis of fats and oils, requires a halogenation period of only 30 minutes, during which time substitution is negligible or absent. This method, on the other hand, is quite incapable of determining the unsaturation of compounds such as cinnamic acid or crotonic acid. In the analysis of the rubber hydrocarbon, Kemp (13), using the Wijs reagent, was able to avoid substitution by halogenating at 0°. Of the iodine-halide methods that of Marshall (24), using iodine chloride and iodine bromide in carbon tetrachloride solution, appears to be more vigorous than similar methods using other solvents, and both permit determination of the halogen used in substitution.

The bromination methods, in contrast with the preceding, are probably considerably more efficient for saturation of multiple bonds (4b,4c,5), but are characterized generally by much more extensive substitution. In the course of this work very few compounds treated with bromine in excess failed to consume bromine in this way, and in some cases substitution was excessive. This seems a priori not to be a serious difficulty in view of the fact that the extent of the substitution is determinable by the device described by Allen (20), first

applied by McIlhiney (4a) and improved by Schweitzer and Lungwitz (31).

In *McIlhiney's Method* the sample, in an iodine flask, is treated with a measured excess of a standard solution of bromine in carbon tetrachloride. After a suitable interval (30 minutes to 18 hours) potassium iodide solution is introduced and the liberated iodine, equivalent to excess bromine, is titrated with standard thiosulphate. There is then introduced a solution of potassium iodate (31) and the liberated iodine, equivalent to the hydrogen bromide of substitution, is titrated. The total bromine consumed, less twice that represented by the second titration, is that taken up by addition.

Addition of iodine chloride, while ordinarily rapid, is retarded by proximity of "negative" groups (*e.g.*, C_6H_5- , –COOH) but Böeseken and Gelber (23) have found it to be complete when the halogenation period is extended (up to 8 hours). Moreover, addition of iodine chloride in dissociating solvents such as acetic acid, is a reversible reaction, especially if the double bond is placed alpha-beta with respect to a negative group. This reversibility is absent when carbon tetrachloride is the solvent, a fact which constitutes a point of superiority for methods using it.

With a solution of iodine chloride in carbon tetrachloride Marshall (24) was able to obtain correct values for compounds, such as cinnamic acid and crotonic acid, not analyzable by other available halogenation methods. Johansen (6), using a solution of iodine bromide in carbon tetrachloride, was able to obtain with petroleum products results in general more satisfactory than those by the Wijs solution.

The addition of bromine is probably similarly affected by presence of negative groups, time, and identity of solvent. Remington and Lancaster (5) found that bromine is superior to the other agents as regards activity in effecting addition. Williams and James (25) found that addition of bromine to unsaturated acids in carbon tetrachloride (in the dark) is catalyzed by formation of a little hydrogen bromide, and to a less extent by hydrogen chloride or water, and that the rate of addition is influenced by the location of the double bond with respect to –COOH or other negative groups. Davis (26) found addition of bromine to olefines in carbon tetrachloride to be strongly catalyzed by light and by moisture, and to be favored by low temperature. He comments upon the difficulty of removing every trace of water from carbon tetrachloride, so that catalysis by moisture is probably common. As will be shown later, certain

unsaturated acids which are resistant to bromination in the cold can be completely and rapidly saturated at 75°. (Fumaric and maleic acids, however, resisted saturation by bromine, and have apparently not been found susceptible to analytic halogenation.)

The evidence appears to justify the belief that saturation by halogen will in general be complete under proper conditions as regards time, temperature, solvent, etc. The results of analysis, however, may fail to show whether or not the saturation was initially complete. A discussion of this point involves consideration of the errors (other than incomplete saturation) which may affect determinations of unsaturation by halogenation methods.

Methods such as those of Hübl, Wijs and Hanûs which do not permit determination of the extent of any substitution which may occur, may often give addition results which are too high. The error is perhaps not often large, and in many cases may be made negligibly small by shortening the halogenation period or by reducing the temperature, as already indicated. Under such conditions, however, the possibility of incomplete halogenation (an error to which such methods are normally liable in certain cases, for reasons already mentioned) is increased. In the general application of these methods, if conditions are such as to insure complete halogenation, the assumption that no substitution occurs is not necessarily valid. These facts constitute a weakness in all methods which afford no facility for determining the amount of halogen consumed in substitution.

Other causes which may lead to high results have not been carefully studied. They include: oxidation by HOX (42,a) (formed by contact of iodine chloride, iodine bromide or bromine with water) or by iodate; the possible rupture of a bridge or chain, followed by halogenation of the free ends; the formation of perhalides (42,b).

The most serious and confusing irregularities which affect halogenation methods are those which lead to low results for addition. Several of these will be discussed:

(1) *Dehalogenation of Metallic Iodide*

Finkelstein (43) showed that chlorine or bromine may be replaced by iodine on contact with sodium iodide (in acetone), especially

when the halogen-bearing carbon is attached to carbonyl, carboxyl, or phenyl groups. In the case of 1,2 –di-iodides formed in this way, loss of iodine occurs, with the introduction of a double bond. Biilmann (41) extended this work, and Van Duin (22) found the reaction to be general as regards alpha-beta–dibromo-compounds: $R.CHBr.\ CHBr.R^1 + 2\ KI \rightarrow R.CH = CHR^1 + I_2 + 2\ KBr$. The tendency to such dehalogenation is determined in part by the nature of the neighboring groups, radicals such as C_6H_5–, –COOH, CH_3CO–, –COOR increasing the rate of the reaction, and bromine retarding it. Böeseken and Gelber (23) studied the same reaction following addition of iodine chloride to double bonds, the resulting alpha-beta chloro-iodo compounds splitting out iodine on contact with potassium iodide:

$$>CCl\,.\,CI<\xrightarrow{KI}>CI\,.\,CI<\longrightarrow>C=C<+\,I_2.$$

(2) *Cleavage of Hydrogen Halide from Alpha-Beta Halogenated Acids*

Böeseken and Gelber (23) found further that addition of iodine chloride to alpha-beta-unsaturated acids in acetic acid results in an equilibrium between the alpha-beta-chloro-iodo acid and its alpha-iodo-beta-lactone: $R\,.\,CH\overline{|Cl|}\,.\,CHI\,.\,COO\overline{|H|}\longleftrightarrow R\,.\,\underset{|____O____|}{CH\,.\,CHI}\,.\,CO + HCl$. During the halogenation the chloro-iodo compound is stable and scarcely any lactone is present, but on addition of water, which opens the beta-lactone ring, reaction occurs as shown. In a method such as McIlhiney's, this will lead to low results.

(3) *Influence of Water*

It is a feature common to all halogenation methods so far considered that the halogenated sample must be brought into contact with water to complete the analysis. This may interfere, as shown above, with analysis of unsaturated acids. Simple hydrolysis, with replacement of halogen by hydroxyl, and reversible formation of hydrogen halide, will interfere with the analysis only in the case of methods in which the hydrogen-halide of substitution is determined. That hydrolytic action occurs has been variously suggested, *e.g.,* by Ingle (28) and by Johansen (6), though Biilmann (41) denies that hydrolysis occurs in the case of 1,2 –dibromo-acids. It will be shown

in the experimental part of this paper that, in the method of McIlhiney, error due to hydrolysis is definitely indicated in several cases, but fails to appear in others in which from structural considerations it might be expected, and that in general hydrolysis is only occasionally a demonstrable source of serious inaccuracy. The indications that it occurs rather generally seem to be fairly definite, but its extent is apparently in most cases slight. This may be due to the low water solubility of most halogenated compounds.

It is possible also that in the analysis of unsaturated esters, partial hydrolysis might occur, assisted by presence of any hydrogen halide formed by substitution. This would liberate acid in the solution, and might lead to error in a method of the McIlhiney type. This point has not been tested sufficiently to admit of generalization, but the few cases examined showed no abnormality attributable to hydrolysis.

(4) *Presence of Acidic Function in the Compound Analyzed*

When substances which contain acid groups are analyzed by a method such as that of McIlhiney, the results will be affected to whatever extent the halogenated sample is itself able to disengage iodine from iodide-iodate solution.

As the acid strength is increased by halogenation, interference due to this cause might be rather generally anticipated, and was found to be strongly operative in several instances. The slight water-solubility of halogenated acids of fairly high molecular weight no doubt limits their effective acidity, and several such compounds were found to show no marked acid-effect in contact with iodide-iodate solution.

The superiority of the bromination methods has been asserted by several chemists (5,6,12,17), but on the whole has not been confirmed by experience (7,8,9,10,11,13,14,15,16,18,19), the Hübl and especially the Wijs methods being rather widely preferred (7,8,9,11, 35,36). McIlhiney's method, however, is perhaps the best general method of bromination (27). It possesses as distinct advantages the irreversibility of halogenation in carbon tetrachloride, the activity of bromine in saturation of double bonds, and the provision which is made for determination of the hydrogen bromide of substitution. It

is, however, open to error from all the general causes mentioned above, of which (1) involves dehalogenation by potassium iodide, and (2), (3), and (4) involve liberation of excess acid in the solution, all leading to low results. The production of more hydrogen bromide than corresponds to the initial substitution is shown later to be a frequent source of error in McIlhiney's method. The tendency for this to occur is increased by extensive substitution, and in McIlhiney's method bromination, both by addition and by substitution, is often exhaustive. The seriousness of the error introduced into the results for addition when liberation of hydrogen bromide is for any reason increased will be appreciated when it is pointed out that the value derived from the hydrogen bromide measured is multiplied by two, and then subtracted from the total bromine consumed. Any cause which increases the production of hydrogen bromide will, therefore, disproportionately decrease the indicated addition, which is a derived value, only the values for total bromine consumed and for hydrogen bromide liberated being actually measured.

Experience with the method of McIlhiney applied to pure unsaturated compounds has shown the results for addition to be sometimes too low. This may be due to incomplete addition of bromine at points of unsaturation, and in some cases such incomplete saturation has been shown even after an 18-hour bromination with an excess of bromine not less than 100 per cent.

There is now available satisfactory proof, however, obtained by use of the new procedure described later, that in a number of instances calculated addition-values are too low even though addition of bromine is strictly quantitative. It is noticeable in such cases that the total consumption of bromine is nearly always more than sufficient to account for the unsaturation actually present, but that the calculated addition-value becomes too low when correction is applied for the hydrogen bromide found. Excessive liberation of hydrogen bromide is clearly shown in certain analyses which yield *negative "addition-values," i.e.,* the hydrogen bromide found, when multiplied by two, indicates the bromine substituted to be more than the total bromine absorbed. Johansen (6) obtained meaningless results of this kind with several petroleum products, and the experimental work described below has shown that a number of organic

compounds, both saturated and unsaturated, yield negative addition-values by McIlhiney's method as ordinarily applied.

So far as has been indicated hitherto, the causes for low addition-values, following initially complete saturation by halogen, all depend upon the presence of water and agents added to complete the analysis, viz.: potassium and iodide and iodate. This belief led to a consideration of possible means by which the excess bromine and the hydrogen bromide of substitution may be determined without contact of the sample with water, etc., at any time. To this end there was undertaken the development of an *aeration-procedure,* by means of which it would be possible to eliminate interferences connected with presence of aqueous reagents in contact with the brominated sample. It was expected that this might at once remove all serious abnormalities, and lead to satisfactory results. That it did not in all cases do so is due to an interference which had previously been confused with the sources of error already mentioned. The aeration-procedure, by eliminating at one stroke all irregularities due to water, revealed clearly a source of error which operates to render too low the indicated addition-values of certain compounds, and even to make these values negative. This interference is the secondary cleavage of hydrogen bromide following or during exhaustive analytical bromination.

A description of the aeration-procedure, and a report of the findings obtained by its use, are given below.

II. Aeration Method for Determination of Unsaturation by Bromination

Principle. Bromination by a solution of bromine in carbon tetrachloride is effected in an evolution-apparatus such as that recommended for use in Bunsen's method (40), the temperature being maintained at any desired point from 0° to about 75°. Excess bromine and hydrogen bromide of substitution are blown out by a stream of nitrogen, collected in a solution of potassium iodide, and determined by titration as in McIlhiney's method. Except in the case of very volatile compounds this procedure avoids contact of water with the sample. A few compounds (octylene, trimethyl pentane, and a cracked gasoline) among those examined were carried

more or less completely into the receiver; in such cases the aeration procedure is without the advantage mentioned, and is in the end identical with McIlhiney's method. In most cases evidence was obtained to show that the sample did not leave the flask, some of the brominated products being recovered and identified.

About 40 organic substances, mostly pure or partially pure single compounds, of various classes, and both saturated and unsaturated, were examined by the aeration procedure, at about 75°, at room temperature (20°-25°), and at 0°. Comparative duplicate analyses were in all cases made by the method of McIlhiney, conducted at room temperature, the bromination being continued for 18 hours.

Apparatus and Reagents

I. Materials

(*a*) *Bromine-Carbon Tetrachloride Solution.* (0.28 N — 7 cc. bromine per liter carbon tetrachloride).

It was found that the best grades of carbon tetrachloride procurable, if not previously purified, consumed appreciable quantities of bromine under the conditions of the bromination. The bromine-combining impurity was removed by refluxing the carbon tetrachloride, in three liter lots, for several hours with one per cent its weight of bromine, removing the excess bromine with sodium carbonate solution and, after contact with calcium chloride for twenty-four hours, distilling through a five-ball Snyder column, discarding the first and last 100 cc. of the distillate. The resulting carbon tetrachloride consumes no bromine on heating to 75°.

A very satisfactory method of measuring the bromine-carbon tetrachloride solution is to fill the 25 cc. automatic pipette by use of pressure. The procedure to be used will be evident upon examination of Fig. 1. This avoids the inconvenience and possible danger involved in filling the pipette in the ordinary way, which was found also to involve a small loss of bromine (equivalent to about 0.02 cc. of 0.2 N sodium thiosulfate).

Standardization of Bromine Solution

Into an iodine flask containing 150 cc. of 15 per cent potassium iodide solution, pipette 25 cc. of the bromine-carbon tetrachloride

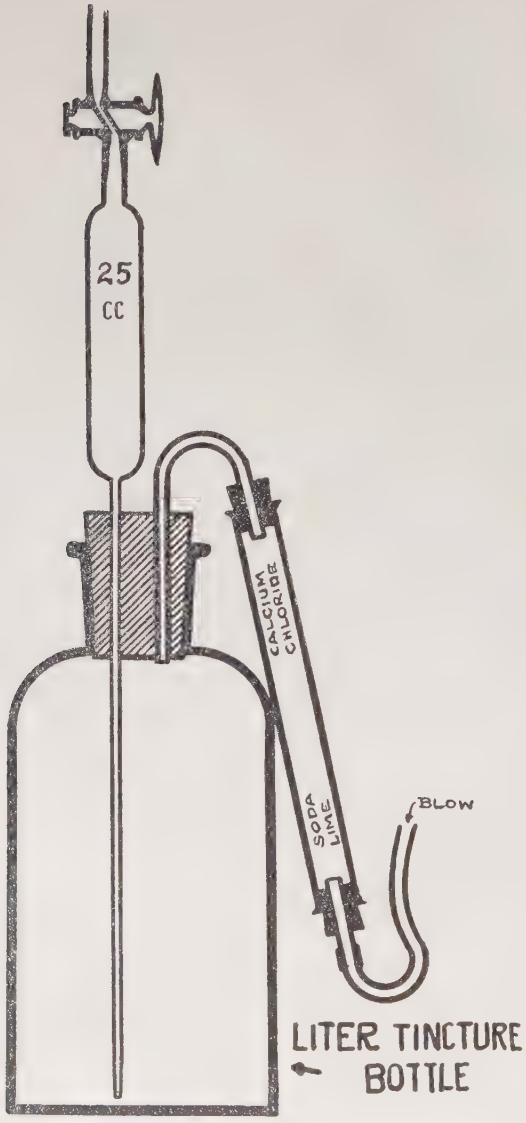
25
CC
CALCIUM CHLORIDE
SODA LIME
BLOW
LITER TINCTURE BOTTLE

FIG 1

solution and immediately titrate the liberated iodine with 0.2 N sodium thiosulfate solution in the usual way. Then add 10 cc. of 2 per cent potassium iodate and titrate any iodine which may be liberated. This titration was in all cases either zero or very small (0.03–0.05 cc.). Vigorous shaking near the end of the titrations is necessary in order to remove last traces of iodine from the carbon tetrachloride. The loss of strength per day when the bottle is rather frequently opened is about 0.2 per cent.

(*b*) *Sodium Thiosulfate* (0.2 N).

This solution, containing 50 grams of the salt per liter, was prepared in the usual way and standardized against pure potassium iodate (McNabb and Wagner, Ind. Eng. Chem., Anal. Ed *I*, 32 (1929)).

(*c*) *Potassium Iodide* (iodate-free). 15 per cent solution.

(*d*) *Potassium Iodate.* 2 per cent solution.

(*e*) *Starch Solution.* 0.5 per cent solution of soluble starch.

(*f*) *Nitrogen, cylinder.*

II. Procedure

Brominations were carried out at three temperatures

(a) 0° (b) 20°-25° (c) 70°-75°

As only slight modifications of a general procedure are required for the brominations at these various temperatures, the former will be described first.

General Procedure

Put into receiver (A), Fig. 2, 100 cc. 15 per cent potassium iodide solution and into trap (B) 10 cc. of the same solution together with about 0.5 cc. standard sodium thiosulfate solution, the last accurately measured from a burette. Introduce the sample into the bromination flask (C), dissolve in 5 cc. carbon tetrachloride and assemble the apparatus as shown in figure. Introduce 25 cc. of standard bromine solution into the flask by means of the automatic pipette, the tip of the latter being thrust well into the constriction of the funnel (D). A gentle suction applied at the trap quickly draws the solution into the flask without loss of bromine. Pass nitrogen immediately through the apparatus at the rate of 20 bubbles per minute and continue this rate until it is desired to begin the

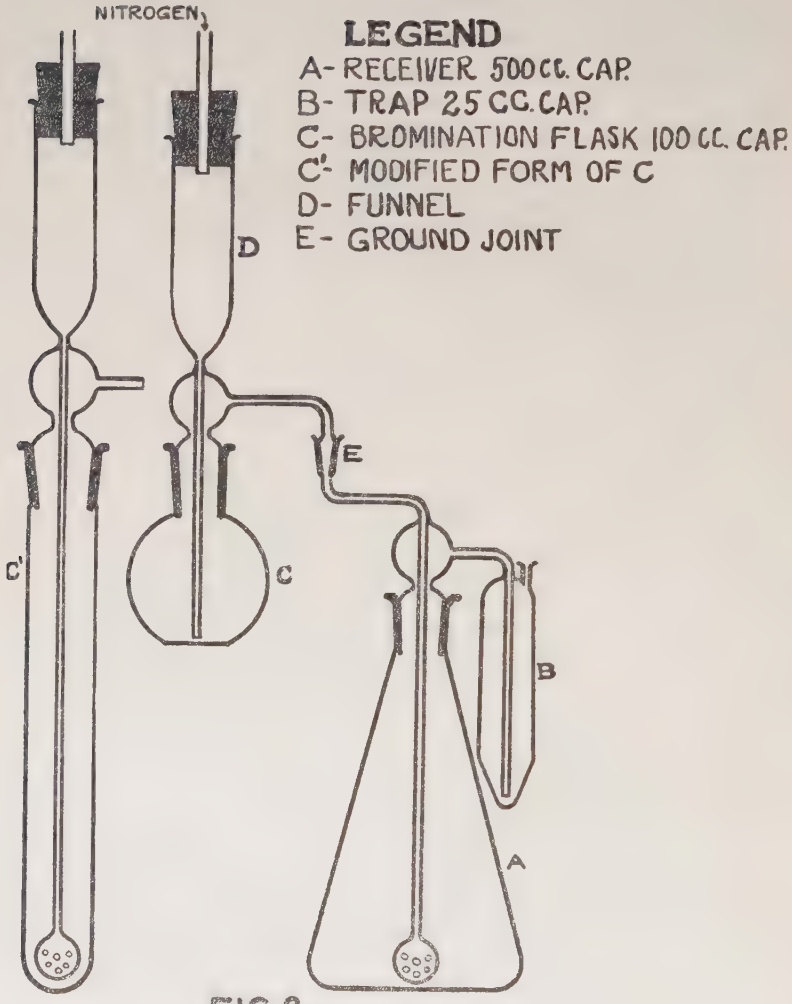
NITROGEN
LEGEND
A- RECEIVER 500 CC. CAP.
B- TRAP 25 CC. CAP.
C- BROMINATION FLASK 100 CC. CAP.
C'- MODIFIED FORM OF C
D- FUNNEL
E- GROUND JOINT
D
E
C'
C
B
A

FIG 2

transfer of bromine, etc., to the receiver. During this time only a small amount of bromine is carried over into the receiver so that the bromination may be considered as of this duration.

At the end of the bromination period, increase the flow of gas to about 150 bubbles per minute in order to transfer the excess bromine and hydrogen bromide of substitution as rapidly as possible into the receiver. Disconnect the apparatus at (E) transfer the contents of the trap to the main receiver and make titrations for excess bromine and hydrogen bromide.

Modifications of General Procedure

(*a*) *Bromination at 0°.*

In this case the bromine solution must be cooled to 0° before contact with the sample. Assemble the apparatus (Fig. 2) and surround the reaction flask with crushed ice. Add standard bromine solution in the manner outlined above, and when chilled to 0° (during the 15 minutes allowed for chilling a slow flow of nitrogen is passed through) introduce the sample, weighed in a glass cup or bulb, into the funnel and wash into the flask with a small amount of cold carbon tetrachloride.

(*b*) *Bromination at 20°-25°.* See general procedure.

(*c*) *Bromination at 70°-75°.*

This differs from the general procedure in that after the addition of bromine solution to the sample, the flask is immersed in a water bath heated to 75°, care being taken to keep the level of the water below that of the bromine solution. Carbon tetrachloride must be added from time to time to prevent distillation to dryness.

The time required for the analysis is roughly as follows:

At 0°	7 hrs.
At 20°-25°	3½ hrs.
At 70°-75°	1½ hrs.

Calculation of Results

The amount of the bromine used for addition is obtained by subtracting double the amount of bromine found as hydrogen bromide by the second titration from the total amount of bromine used as determined by the first titration.

Procedure for Comparative Trials by Method of McIlhiney

The weighed sample, in a small glass cup, or a thin glass bulb in case the substance was volatile, was introduced into a dry 500 cc. iodine flask and dissolved in 10 cc. of purified carbon tetrachloride. There was added, from an automatic pipette, 25 cc. of about 0.28 N bromine in purified carbon tetrachloride, and the stoppered flask was allowed to stand for 18 hours at 20°-25° in a shadowed place. Four or five analyses were run in each series, and also a blank analysis by means of which the effective strength of the bromine solution was ascertained. The flask was immersed in ice water, 10 cc. of 25 per cent potassium iodide and about 5 cc. water introduced in the usual way, and the flask shaken up and down to dissolve bromine and hydrogen bromide present in the vapors. The flask was opened, the stopper washed, about 25 cc. water added, and the free iodine titrated with 0.2 N sodium thiosulfate, using starch indicator. Near the end of the titration the flask was stoppered and shaken frequently to dissolve iodine from the carbon tetrachloride. The end-point of this titration was almost invariably sharp. There was then added 10 cc. of 2 per cent potassium iodate solution, and after a minute the liberated iodine was titrated in the same way. The end-point was in many cases somewhat uncertain due to return of the blue color.

Comparative Results by Aeration Procedure and by McIlhiney Method

The comparative trials by the two procedures are grouped below according to the general type of compounds examined, or according to the nature of the point to be tested. Results give total bromine absorbed, bromine substituted, and bromine added, in terms of atoms of bromine per molecule; addition is expressed also as percentage of bromine absorbed, with the calculated equivalent iodine number included in some cases for comparison. Check analyses by McIlhiney's procedure do not represent duplicates run in the same series, but duplicates run on different days.

It is to be emphasized as important, in judging the findings by the aeration procedure, that results by McIlhiney's method are believed to be the best available basis of comparison, this method being

accepted as the present bromination standard. Any superiority shown by the aeration procedure, even though the deviations from theory are still relatively large, is to be viewed as an improvement.

The apparent accuracy of results is in many cases less than the manipulative accuracy. This is especially true of analyses in which relatively small samples were used, the error appearing most conspicuously in the calculated percentage of bromine, which represents often a considerable magnification of the analytical figures. It is frequently the case that results of several per cent in the Br-addition columns actually represent titrations of only a drop or two. On the other hand it is true that statement of results in terms of atoms of bromine per molecule of sample, while it facilitates rapid interpretation of the bromination values, certainly tends to conceal the analytical errors.

Attention is called first to the marked influence of temperature upon the results obtained by the aeration procedure applied to cyclohexene, phenanthrene, retene, and indene. Variations of temperature have not received much attention from investigators of bromination methods, most of which are adapted only to lower temperatures, and are almost always conducted at room temperature. (Cf. Kemp (13), and Davis (26) .)

Operation at 75° greatly reduces the time required for transferring the excess bromine and the hydrogen bromide into the receiver, and when this temperature is without undesirable effect upon the results, it is distinctly preferable to the slower procedures at lower temperatures. Consideration of some of the results in the tables, however, shows clearly that at 75° certain compounds yield low results, which become higher by lowering the temperature of analyses. This behavior is by no means restricted to the compounds named above, but has been encountered rather frequently. An extreme case that of retene, which at 75° yields a negative value for addition, whereas at 0° the value is positive and normal. This behavior is shown also by other compounds to be considered later and its interpretation is a matter of importance in a study of analytic bromination. A discussion of the significance of negative addition-values and of their tendency to become positive when the temperature of

TABLE I

UNSATURATED HYDROCARBONS

Compound	Aeration Method						McIlhiney Method				Theoretical Br. No.	Remarks
	Temp.	Time Hrs.	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added		
Octylene (B. p. 123.3° c.)	60°	¾+1	2.27	0.15	1.98	140.9	2.72	0.42	1.87	133.5	142.5	
	20°	1+4	2.13	0.07	1.98	141.2	2.65	0.36	1.93	137.2		
Cyclohexene (B. p. 82.0° c.)	75°	1+½	2.12	0.17	1.77	172.7					194.7	
	75°	2+½	1.99	0.11	1.77	172.7						
	20°	½+5	2.04	0.07	1.90	185.2	2.15	0.19	1.78	173.3		
	0°	1+8	1.99	0.03	1.93	187.6	2.08	0.12	1.85	180.1		
Limonene (B. p. 176.6° c.)	75°	1+½	5.55	0.72	4.10	240.4	4.60	0.31	3.98	233.6	234.7	
	75°	1+½	4.88	0.39	4.11	241.0	4.68	0.35	3.97	233.1		
Styrene (B. p. 146.0° c.)	75°	4+½	2.04	0.00	2.04	157.0	1.96	0.02	1.92	147.4	153.5	Dibromide isolated M. p. 73°
							2.07	0.02	2.03	155.9		
Stilbene (M. p. 124.0° c.)	75°	1+½	2.01	0.00	2.01	89.2	2.02	0.02	2.00	88.7	88.7	Dibromide isolated M. p. 236.5°
	75°	1+½	2.00	0.00	2.00	88.7			2.02	89.7		
	75°	1+½	2.00	0.00	2.00	88.7			2.00	88.7		
Phenanthrene (M. p. 99.7° c.)	20°	½+6	2.55	0.44	1.68	75.2	3.31	0.79	1.73	77.6	89.7	
	0°	3+7	2.88	0.43	2.02	90.8	2.79	0.47	1.85	82.9		
Retene (M. p. 97.5° c.)	75°	1+½	7.14	3.73	—0.34	—11.8	6.25	2.23	1.79	61.1	68.2	
	0°	3+7	5.75	1.89	1.97	67.0	8.00	3.19	1.62	55.3		
Indene (B. p. 182.8° c.)	75°	1+½	4.13	1.21	1.69	116.5					137.7	
	25°	0+5	2.17	0.17	1.82	125.1	3.91	1.07	1.76	121.3		
	0°	2+5	2.26	0.22	1.81	124.4	4.29	1.26	1.75	120.6		
	0°	½+7	2.32	0.21	1.89	129.9						

bromination is lowered is withheld until other examples have been presented.

In addition to revealing the temperature effect referred to, the aeration method proved to be (for optimum temperature) generally more accurate than McIlhiney's, the results being in most cases distinctly nearer the theoretical.

(1) The Determination of Unsaturation of Hydrocarbons

In Table I there are given results obtained by the two procedures applied to the analysis of some olefinic compounds. Table II records results obtained with technical hydrocarbon mixtures obtained from petroleum.

Table II

Petroleum Products

N.B.—For convenience in comparison, the bromine values obtained are all reported as the equivalent iodine values.

	Aeration Method					McIlhiney Method			Johansen Method ½ Hr. Bromination Results by Refinery Lab. (Quoted)	
Sample	Temp.	Time	≏ % Iodine Total	≏ % Iodine Subst.	≏ % Iodine Added	≏ % Iodine Total	≏ % Iodine Subst.	≏ % Iodine Added	≏ % Iodine Subst.	≏ % Iodine Added
Heavy Lubricating Oil	75°	1+½	67.8	38.3	—8.2					
	75°	2+½	55.1	19.1	—5.5	63.8	35.3	—6.8	10.9	—1.5
	23°	1+3	33.6	16.4	+0.9	44.2	23.2	—1.7		
	0°	1+7	27.2	12.5	+2.2	45.4	23.5	—1.8		
Transformer Oil	75°	1+½	62.5	34.6	—6.8	64.8	35.1	—5.1	8.3	—0.05
	25°	1+3	21.0	10.5	—0.1	60.0	32.2	—4.4		
	0°	1+7	15.0	7.1	+0.9					
Cracked Gasoline Fraction	60°	1+½	118.2	43.4	31.3	144.8	53.2	38.4	23.5	32.8
	20°	1+8	84.8	25.1	34.7	154.0	58.4	37.3		
	0°	1+6	67.3	14.7	37.8					

Discussion—Negative values obtained for the first two samples by the ordinary procedures are by the aeration procedure made more negative at 75°, but become positive and perhaps normal at 0°. A similar temperature effect, less conspicuous because it involves no change in sign, will be noticed for the

third sample. The above results show the possibility of avoiding negative addition-values, which are the most unsatisfactory obtainable because of the absence of any reasonable meaning which can be attached to them. There seems to be no reason why either the McIlhiney, the Johansen, or any similar method might not escape this difficulty if conducted at low temperature.

(2) Determination of Unsaturation of Compounds with Acidic Function

It was mentioned previously that the second titration (after addition of potassium iodate) intended to indicate the hydrogen bromide of substitution, will equally well show acidity due to other causes. The presence of an acidic function in the substance examined may therefore constitute an obstruction to the analysis, for the acid character may be considerably strengthened by bromination. In such cases the acid titration will be too large, and the addition-values will be too low by double this error. There will, of course, be cases when the acidic sample will register quantitatively its acidity, for which deduction may then be made in the calculation. More often, however, the acidity is of a relatively low order, even after bromination, and will presumably introduce an indeterminate error. Such an interference is sometimes suggested by the observation that the end-point of the acid titration is more than usually impermanent, the color returning rapidly, strongly and persistently. Continuation of the titration at intervals until a permanent end-point was finally reached has in some instances yielded apparent hydrogen bromide values which have almost completely cancelled the original total bromine-absorption, making it appear that nearly all the bromine introduced has been split out as hydrogen bromide. Combined with the foregoing cause of irregularity in the bromination of acidic substances there is also the possibility that separation of bromine as hydrogen bromide may be favored (especially if bromination has occurred in a part of the molecule near the acidic function) by the somewhat increased reactivity of halogen when present in such compounds. The secondary elimination of bromine hydrolytically, or by action of potassium iodide (Van Duin, Boeseken and Gelber), or of hydrogen halide from halogenated unsaturated acids, due to formation of lactones or to double-bond formation, are all possible, and would all lead to low addition-values.

Certain of the interferences mentioned are contingent upon presence of water, potassium iodide, etc., in contact with the brominated sample. They should be eliminated if such contact is avoided. Continued abnormal results must then be due to a more restricted number of possibilities, while improvement in the values obtained will indicate the cause of irregularity to be among the possibilities excluded by the exclusion of water, etc. The aeration procedure obviously permits experimental testing of these considerations, and was accordingly applied to examination of a number of unsaturated acids, in comparison with the method of McIlhiney. Some results are given in Table III.

Discussion

Results for undecylenic acid, oleic acid, and erucic acid are distinctly low by both methods. As the two sets of values are nearly the same, and as examination of the data does not reveal any obvious unfavorable effect due in any case to water, temperature, or time, it is assumed that the results are approximately correct for the material analyzed, all three of the acids being not very pure.

Crotonic acid gave satisfactory results by the aeration method, but McIlhiney's method failed entirely, the indicated total absorption of bromine being very low. Crotonic acid is indicated quantitatively as an acid in contact with potassium iodide and potassium iodate. The titrations following addition of iodate, in the McIlhiney trials, were nearly identical with those calculated on the assumption that the sample reacted simply as an acid, and for this reason the substitution values are set down as zero. It may be added that the Hübl method has likewise been found to fail with crotonic acid,[30] the iodine value being 25.5 instead of the theoretical 294.9.

Crotonic acid affords an excellent example of an acidic compound the determination of whose unsaturation is interfered with by presence of water.

Cinnamic acid is analytically somewhat similar to crotonic acid. Results by the aeration method are satisfactory, substitution being nil. The total consumption of bromine in the McIlhiney method is almost exactly theoretical, and the results would be excellent if the acid titration were ignored. In presence of iodide-iodate solution, however, the sample appears not only to register its full value as an

TABLE III

COMPOUNDS WITH ACIDIC FUNCTION

Compound	Aeration Method						McIlhiney Method				Br. No. (Theory)	Remarks
	Temp.	Time	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added		
Crotonic Acid (M. p. 71.8° c.)	75°	1+½	2.06	0.05	1.96	182.3	0.49	0.0	0.49	45.6	185.7	Dibromide isolated M. p. 86.5°
	75°	1+½	2.07	0.03	2.01	187.0	0.58	0.0	0.58	54.2		
	20°	16+3	0.31	0.00	0.31	22.6						
Undecylenic Acid (M. p. 21-22° c.)	60°	1+½	2.04	0.12	1.80	78.1					86.8	
	22°	1+2	1.99	0.09	1.80	78.2	2.23	0.28	1.67	72.4		
	0°	1+7	1.89	0.05	1.79	77.5	2.13	0.19	1.75	76.1		
Oleic Acid Commercial	20°	1+4	1.99	0.11	1.79	50.5	2.19	0.24	1.70	48.2	56.6	
	0°	1+8	1.89	0.05	1.79	50.7	2.19	0.23	1.73	48.8		
Fumaric Acid	75°	1+2	nil					nil				
Maleic Acid	75°	1+2	nil					nil				
Erucic Acid (M. p. 31-32° c.)	70°	1+½	2.56	0.51	1.54	36.3	3.03	0.70	1.64	38.7	47.2	
	70°	0+1	2.45	0.38	1.70	40.1	2.37	0.33	1.72	40.6		
	20°	15+3	2.5	0.4	2.1	49.6						
Cinnamic Acid (M. p. 133° c.)	75°	1+½	2.02	0.00	2.02	109.1	2.00	1.09	—0.19	—9.9	107.9	Dibromide isolated M. p. 193.0°
	75°	1+½	2.02	0.00	2.02	109.2	1.99	0.97	+0.05	2.5		
Abietic Acid (M. p. 155° c.) Prepared from Florida Rosin	75°	2+½	10.1	6.70	—3.34	—88.1					For 1 double bond, mol. wt. 302: 52.9	
	75°	1+½	10.37	6.03	—1.69	—44.8						
	75°	0+½	7.34	3.81	—0.30	—7.8						
	0°	0+7	4.98	1.65	1.68	+44.3						
	0°	1½+8	6.06	1.87	2.33	+61.6	10.87	6.56	—2.24	—59.4		
	0°	1+7	6.96	2.48	1.99	+52.5	9.72	5.37	—1.02	—27.1		
			%	%		%	%	%		%		
Rosin (Florida)	75°	1+½	265.4	154.9		—44.4						
	20°	1+4	187.9	84.8		+18.3	292.7	173.3		—53.8		
	0°	1+7	155.0	61.8		+31.4	285.7	163.8		—41.9	Nil*	

*according to McIlhiney (J.A.C.S. *16* 275) (1894).

acid, but also to undergo a fairly rapid and complete hydrolytic breakdown, such as is known to be characteristic of cinnamic acid dibromide.* The initial iodate titrations represented approximately the acid-values of the samples (10.48 cc. instead of 9.57; 6.97 cc. instead of 7.16 cc.), and the end-point of the titration was exceedingly poor, the color returning almost instantly, and strongly.

The extent of the secondary hydrolytic decomposition was determined approximately by allowing these analyses, and their accompanying blanks, to stand for a further period with occasional shaking, the liberated iodine being titrated at intervals. In the case of the first sample the main and the blank supplementary titrations became identical after 11 days. The total acid titrations were then 0.90 cc. of thiosulfate (0.1615N) for the blank and 28.53 cc. for the analysis, the difference of 27.63 cc. representing the total iodine liberated by contact of the brominated sample with iodide-iodate solution. Deducting the 9.57 cc. attributable to the carboxyl group, the titration representing the extent of hydrolytic decomposition is 18.06 cc. As the total bromine originally absorbed corresponds to 19.19 cc. it is obvious that the decomposition was nearly complete, practically all the bromine introduced being returned to the solution.

Cinnamic acid therefore affords another example of the interference of water. If the use of iodate is omitted, cinnamic acid is actually analyzable by McIlhiney's method, but only because it so happens that substitution entirely fails to occur. The method of Hübl was found to fail with cinnamic acid,[80] the iodine-values ranging from 15.3 to 16.4 instead of the theoretical 179.4. The aeration method, on the other hand, is applicable in its most rapid form (75°), and would be equally serviceable for cases in which substitution occurs.

Abietic Acid

It was in the course of an attempt to determine the unsaturation of abietic acid that the aeration procedure was first used. Attempts to obtain satisfactory results by McIlhiney's method gave such apparently clear indications of the interference of water that it was decided to operate in absence of water. The results given in the table above, however, do not admit a certain conclusion that water is mainly responsible for the large negative values obtained by the McIlhiney method. At higher temperatures, and in absence of water,

*Beilstein 4th Ed. *IX* P-518.

the aeration method gave negative values as large as those by McIlhiney's. At low temperature, however, the aeration procedure yielded the most surprising and significant results yet obtained, the large negative values referred to being replaced by positive addition-values indicating roughly one double bond in the molecule of abietic acid. The improvement between 75° and 0° is relatively enormous and it is certainly possible that the highest addition-value obtained is still a partial one, a temperature of 0° being perhaps too high.

Throughout the results by the aeration procedure the effect of time will be observed to be fairly marked, a relatively brief bromination being apparently able to saturate the double bond, and tending to reduce substitution and hence also complications which seem to accompany it when extensive. The use of short bromination periods, however, while desirable as a means to restrict substitution, may lead to incomplete saturation, and is therefore not a safe general procedure. The saturation of double bonds in compounds which contain negative functions meets a certain amount of resistance, especially when the two functions are in proximity, and requires longer periods of bromination. Some of the addition results in Table III are in all probability too low due to insufficient time allowed for bromination. This tendency toward low addition-values is perhaps related to the extent of the substitution, this important consideration being discussed later.

Rosin

McIlhiney originated his method (4a) for the determination of rosin in commercial products. He proceeded on the assumption that rosin takes up bromine by substitution only, and may therefore be estimated in presence of other known substances which take it up additively or not at all. The bromine addition-values for rosin as stated by McIlhiney vary from 0 (4a) to about 8% (4b), the substitution values (for a 30-minute bromination) being 65 to 80. The substitution values obtained with this substance, as is well known, will vary with conditions such as temperature, time and excess of bromine.

The material referred to in the table was a Florida winter-rosin of Grade WW(X). As is shown, the total bromine absorbed in

an 18-hour bromination by McIlhiney's method approached 300 per cent, and the indicated addition-values were *negative* and fairly large. Similar negative values were obtained at 75° by the aeration method, but at 20° a 1-hour bromination gave a positive result for addition, and the indicated addition was substantially greater at 0°. If there are compared the results by the two methods at room temperature (+ 18% by aeration, and about –48% by McIlhiney's method) it could be concluded that either the presence of water or the greater time of bromination in some way abnormally increased the apparent hydrogen bromide of substitution obtained in the McIlhiney procedure. On the other hand conclusion that water is the interfering agent is greatly weakened by the fact that in absence of water the magnitude and even the sign of the results is seemingly a function of temperature. An interpretation of these somewhat confusing results is given in a later section.

(3) Bromination of Some Other Compounds

Results for some other compounds of various types are listed in Table IV. The examination of cumene, cymene, and menthane was undertaken mainly to study the behavior of the isopropyl group, since it was thought possible that bromination of its tertiary carbon might yield a condition readily susceptible to hydrolytic removal of bromine, or to cleavage of hydrogen bromide.

Other compounds include several unsaturated esters, examined to study possible error in McIlhiney's method due to slight hydrolysis of ester, after addition of water, by the hydrogen bromide of substitution.

Discussion

The extent of the bromination of menthane in the cold was in all cases slight. The values for addition indicated by McIlhiney's method represent actually very small titrations (0.18 cc., 0.31 cc.), and are probably not of great significance. Results by the aeration method are of interest due to the appearance of negative values whose magnitude is clearly connected with the temperature of bromination. The negative sign disappears for bromination at 0°, the result of 0 at that temperature being normal.

TABLE IV

BROMINATION OF SOME ISOPROPYL-HYDROCARBONS AND OF SOME ESTERS

Compound	Aeration Method						McIlhiney Method				Bromine-number: theoretical
	Temp.	Time	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added	
Menthane (B. p. 169.0° c.)	75°[a]	1+½	4.47	2.41	—0.35	—19.9					0.0
	30°		3.56	1.88	—0.21	—12.0					
	25°	16+4	1.94	0.10	—0.04	—2.3	0.23	0.08	0.06	3.2	
	0°	2+6	0.05	0.02	+0.02	+0.1	0.09	0.00	0.09	5.3	
Cumene (B. p. 153.3° c.)	75°	1+½	4.37	2.18	0.01	0.5	3.99	1.94	0.09	5.9	0.0
	20°	1+4	5.82	2.86	0.08	5.1	4.02	1.88	0.05	3.6	
Cymene (B. p. 153.3° c.)	75°	1+½	6.35	3.14	0.06	3.6	4.77	2.74	—0.73	—43.4	0.0
	0°	1+5	4.77	2.36	0.05	2.9	3.80	2.18	—0.58	—34.5	
Ethyl Fumarate (Eastman)	75°	1+½	1.98	0.01	1.96	90.9	1.02	0.0	1.02	47.3	92.9
	20°	½+5	2.03	0.00	2.03	94.3	1.33	0.0	1.33	61.5	
Ethyl Maleate (Eastman))	75°	1+½	1.89	0.17	1.55	72.0	1.80	0.09	1.61	74.9	92.9
	20°	½+5	0.65	0.01	0.63	29.5	1.45	0.04	1.38	64.0	

Cumene, and also *cymene,* appear to have taken up bromine by addition, cumene in both methods, and cymene in the aeration method only. The examination of cymene by McIlhiney's method affords another example of negative results, which in this case are probably due to hydrolytic action. The fact that cumene shows no such behavior suggests that the methyl group, and not the isopropyl group, may be responsible for the abnormality. This supposition is strengthened by the fact that mesitylene also gave negative results by McIlhiney's method, but a result of 0 by the aeration method.

Ethyl fumarate gave satisfactory results by the aeration method but not by McIlhiney's. *Ethyl Maleate* yielded low results, the data indicating that bromination was incomplete, as the total absorption of bromine was less than that required for saturation of the double bond, and as little substitution occurred.

Pinene and Ethyl Oleate. Of the compounds examined only two, pinene and ethyl oleate, yielded addition-values which, though fairly definite, were considerably too high. The results obtained are tabulated below.

The convergence of the results for *pinene,* by both methods, upon a bromine-value corresponding to *three atoms of bromine added,* is striking and probably significant.

Other halogenation methods likewise yield for pinene results that are too high. Ingle (28) obtained a Hübl value of 347 (instead of the theoretical 187), indicating absorption of nearly 4 atoms of bromine. Klimont (29) by a bromide-bromate method similar to that described recently by Francis (12) (but certainly more likely than the latter to cause substitution) obtained a bromine value of 234.2, corresponding to exactly 4 atoms of bromine. These methods of course give merely the sum of addition and substitution, and as the latter occurs rather readily with pinene, it is not surprising that results are higher than that required for one double bond.

Ethyl oleate absorbed additively by both methods close to 2.3 atoms of bromine instead of the theoretical 2 atoms (59% instead of 51.5%). Though this case seems to be similar to that of pinene, no great significance is at present attached to the observed discrepancy, in spite of its regularity, because the ester (Eastman No. 1971, b.p. 205°-208°) was probably not analytically pure.

TABLE V

Compound	Aeration Method						McIlhiney Method				Theoretical Bromine Number
	Temp.	Time	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Added	Atoms Br. Total	Atoms Br. Subst.	Atoms Br. Added	% Br. Total	
Pinene (B. p. 158.8° c)	75°	1½+½	4.85	1.09	2.67	156.5	4.55	0.83	2.88	169.3	117.4
	25°	13+3	4.65	0.89	2.86	167.6	4.80	0.91	2.98	174.9	
	0°	½+7	4.46	0.65	3.16	185.4	4.29	0.63	3.00	176.3	
Ethyl Oleate (Eastman)	75°	1+½	2.78	0.26	2.26	58.3	3.19	0.45	2.30	59.2	51.5
	25°	0+5	2.63	0.10	2.46	62.4	3.02	0.39	2.24	57.6	

(4) The Cleavage of Hydrogen Bromide from Brominated Compounds

A number of the substances examined by the aeration method yielded results which were remarkably affected by temperature, the indicated addition decreasing with higher temperatures of bromination, and even becoming negative in some cases. Lower temperature appeared to favor normal bromination, and was effective in producing useful values with some substances whose bromine numbers at higher temperatures were hopelessly wide of the mark.

It is a conspicuous feature of these abnormal cases that as temperature is raised the extent of the bromination increases greatly, and at higher temperatures (e.g., 75°), *when the indicated addition is at a minimum or is even negative, the amount of bromine introduced is at a maximum.* It is hard to believe that under such conditions any olefinic bond can remain unsaturated by bromine, and even if this rather unlikely possibility is admitted, it would still be impossible thus to account for a negative addition-value, as failure to saturate an olefinic bond would not yield a negative, but merely a zero, value. Whether or not saturation has occurred, a negative addition-value can mean only one thing: *Hydrogen bromide is being produced in excess of that properly considered as hydrogen bromide of substitution.* Since in these brominations the samples at no time came into contact with water, the hydrolytic removal of bromine as hydrogen bromide may be dismissed from consideration. This same condition also excludes debromination by contact with potassium iodide (bromine being first replaced by iodine, and this splitting out to establish an olefinic condition). There remains the conclusion that hydrogen bromide splits out spontaneously because the loading of the molecule with bromine by substitution, a process favored by heat, leads to a condition of instability at the existing temperature.

If this is the correct explanation of low or negative addition-values, then inspection of the analytic data should reveal the fact that such results are associated with extensive substitution. That this is the case for the limited number of examples available becomes evident upon comparison of the substitution value for a temperature at which indicated addition was negative with that for a temperature at which indicated addition was normal.

TABLE VI

RELATIONSHIP BETWEEN EXTENT OF SUBSTITUTION AND HYDROGEN BROMIDE CLEAVAGE

Compound	Temp.	Indicated Addition % Br.	Br Substituted % Br.
Retene	75°	—11.8	255.2
	0°	+67.0	129.0
Abietic Acid	75°	—88.1	354.0
	0°	+52.5	131.6
Rosin	75°	—44.4	154.9
	0°	+31.4	61.8
Menthane	75°	—19.9	274.5
	0°	+0.1	0.2
Heavy Lubricating Oil	75°	—5.2	23.9
	0°	+1.4	7.8
Transformer Oil	75°	—4.3	21.6
	0°	+0.5	4.5

These figures indicate that it was in every case a heavily brominated substance which split out hydrogen bromide other than the hydrogen bromide of substitution. A glance over the tabulated results for compounds which gave good addition-values without special temperature control will show that in such cases the amount of substitution is not more than moderately large, and is usually distinctly small.

Considerations such as the preceding may establish the plausibility of hydrogen bromide cleavage but cannot prove it. To test the correctness of the idea, samples of the above substances, brominated at a lower temperature, were freed from bromine and hydrogen bromide in the usual way, and were then heated for about 30-45 minutes in the aeration apparatus, any volatile products of this operation being collected in potassium iodide solution in the receiver. The solution in the receiver was treated with starch solution (no color, showing no free bromine retained in sample or split out), potassium iodate

was added, and any liberated iodine was titrated. The results fully confirmed the hypothesis stated above: in every case tested, excepting only menthane, a substance exhaustively brominated at a lower temperature yielded up free hydrogen bromide when warmed, abietic acid and rosin brominated at 0° losing hydrogen bromide even at room temperature. The hydrogen bromide obtained was not merely a qualitative trace, but in several cases approximated in amount the excess hydrogen bromide indicated by the abnormal results of analysis at the higher temperature. The following table presents the results of these experiments. The bromine-values represent the ratio

$$\frac{100 \times \text{bromine split out as hydrogen bromide}}{\text{Sample}}$$

The last column shows what part of the total bromine of substitution at lower temperature was split out as hydrogen bromide on warming to 75°.

TABLE VII

CLEAVAGE OF HYDROGEN BROMIDE FROM BROMINATED SUBSTANCES BY WARMING

Substance	% Br out as HBr. 0°-25°	% Br out as HBr. 25°-75°	% Br out as HBr. 0°-75°	% of total Br of subst. at lower temp. split out at 75°
Abietic Acid	—	—	56.1	87.3
	—	—	50.1	100.0
Rosin	—	—	21.0	25.0
	2.3	14.0	16.3	28.9
Retene	0.0	22.0	22.0	60.0
Phenanthrene	0.0	15.0	15.0	77.7
Gasoline	—	0.7	0.7	4.1

The above values do not necessarily represent all the hydrogen bromide which could be eliminated on warming, as no effort was made to complete the action. In spite of this, the hydrogen bromide split out of brominated abietic acid, if multiplied by 2 as in the analysis, and subtracted from the addition-values for 0°, changes these to –59.8 and –38.6, respectively. Similarly the "corrected" results for rosin become –24 and –1.2. The addition value for retene is

reduced from 67 to 23, and that for phenanthrene from 90.8 to 60.8. It is, therefore, shown that abnormal addition-values obtained at higher temperatures may be roughly duplicated artificially by brominating at low temperature and then splitting out hydrogen bromide by warming. When the bromination is effected at 75° the cleavage of hydrogen bromide is probably greater, for the reason that much more bromine has been introduced.

No chemical or physico-chemical explanation of the mechanism of hydrogen bromide cleavage will be attempted. The net result of such action must be the dehydrogenation of the compound by action of bromine, and this involves the introduction of double bonds under conditions suitable for saturating them.

III. General Discussion of Results—Conclusions

To facilitate the discussion which closes the paper there will be gathered at this point the essential results of Tables I to V, inclusive; such iodine-values as have been found in the literature are included in appropriate places. For purpose of comparison these iodine values are stated also as the equivalent bromine-values (Iodine No. x 0.6297). In the case of results by the aeration method, there are selected those obtained under the best temperature conditions. The McIlhiney values are averaged.

Examination of the table shows that in all but a few cases the aeration method yields distinctly better results than McIlhiney's method. By operating the latter at 0° it seems likely that in many cases its accuracy would be improved, but some error must always persist in the case of compounds which after bromination are in any way reactive with water, potassium iodide, or iodide-iodate, including of course compounds containing an acid function. Error due to this cause cannot affect analysis by the aeration procedure. The observed ability of brominated olefines to liberate iodine in contact with potassium iodide solution led Sudborough and Thomas (33) to recommend that titration be started immediately after addition of potassium iodide solution. An annoying feature of the McIlhiney procedure is the end-point of the second titration (following addition of potassium iodate). The starch-blue usually returns rapidly and strongly, and if the liquid is allowed to stand in the stoppered

flask, with occasional shaking and titration (the inevitable oxygen effect being compensated by similar treatment of the corresponding blank), the liberation of iodine may continue for weeks. The invariable return of the starch color is of course due to a reaction which has been in progress from the moment the iodate was introduced, and leads to high results for hydrogen bromide. It may be assumed that this behavior is due to hydrolysis. The presence of potassium iodide and potassium iodate, making irreversible the hydrolytic separation of bromine as hydrogen bromide, would be expected to intensify a hydrolysis which might otherwise be scarcely detectable. To avoid the complications caused by contact of iodide-iodate with brominated sample there might be adopted the recommendation of McIlhiney to separate the carbon tetrachloride before the acid titration is made. This operation was part of the original method, in which hydrogen bromide was titrated with standard alkali, but has apparently never been included in the later procedure using iodate.

The fact that by the aeration method (as also by McIlhiney's) addition-values are sometimes low or even negative has been demonstrated, it is believed, to be due to secondary cleavage of hydrogen bromide from the brominated sample. The action is much increased at higher temperatures, and its immediate cause is probably the excessive bromination by substitution which occurs under such conditions. Whatever may be the relationships among the several variables, it is certain that for some compounds the following contrasting associations exist:

1. Higher Temperatures	Extensive Substitution	Excessive formation of hydrogen bromide	Addition-values low or negative
2. Lower Temperatures	Limited Substitution	Normal or only slightly excessive formation of hydrogen bromide	Addition-values improved or normal

The practical application of these findings to the improvement of bromination methods requires the use of bromination temperatures low enough so that excessive substitution, and therefore the tendency to split out hydrogen bromide spontaneously, are both avoided. Results given above show that some substances brominate normally even at 75°, others at (but not much above) room temperature,

TABLE VIII—SUMMARY OF ESSENTIAL RESULTS

Substance	Theoretical Values		Aeration Method			McIlhiney Method (Average)		Other Methods (**)		
	Atoms of Br.	% Br.	Conditions (Temp.)	Atoms Br. Added	% Br. Added	Atoms Br. Added	% Br. Added	Method	% Iodine	% Bromine
Octylene	2	142.5	20°-60°	1.98	141.1	1.90	135.4			
Cyclohexene	2	194.7	0°-20°	1.92	186.4	1.82	176.7			
Stilbene	2	88.7	75°.	2.00	88.9	2.01	89.0	Hübl	140.6	88.5
								Wijs	135±3	85.0
Styrene	2	153.5	75°	2.04	157.0	1.98	151.7	Hübl	227.	142.9
								Wijs	226.6	142.7
Limonene	4	234.7	75°	4.11	240.7	3.98	233.4	Klimont		232.1
Pinene	2	117.4	0°-25°	3.01	176.5	2.95	173.5	Hübl	347.	218.5
								Klimont		234.2
Phenanthrene	2	89.7	0°	2.02	90.8	1.79	80.3			
Retene	2	68.2	0°	1.97	67.0	1.71	58.2			
Indene	2	137.7	0°-25°	1.84	126.5	1.76	121.0			
Cumene	0	0.				0.07	4.8			
Cymene	0	0.	0°	0.05	2.9	—0.66	—39.0			
Menthane	0	0.	0°	0.02	0.1	0.08	4.3			
Lubricating Oil	?	?	0°		+1.4		—1.2	Johansen	—1.5	—0.9
Cracked Gasoline	?	?	0°		23.8		23.8	Johansen	32.8	20.7
Transformer Oil	?	?	0°		+0.5		—3.0	Johansen	—0.05	—0.03
Crotonic Acid	2	185.7	75°	1.99	184.7	0.54	49.9	Hübl	25.5	16.1
								Hanûs	8.	5.
Undecylenic Acid	2	86.8	0°-60°	1.80	77.9	1.71	74.3	Hübl	123±2***	77.5
								Wijs	133.1	83.8
Oleic Acid, U.S.P.	2	56.6	0°-20°	1.79	50.6	1.72	48.5	Hübl	85.0	53.5
								Hanûs	84.2	53.0
Fumaric Acid	2	137.9	20°-70°	0.	0.			Hübl	0.	0.
								Wijs	0.	0.
Maleic Acid	2	137.9	20°-70°	0.	0.			Hübl	0.	0.
								Wijs	0.	0.
Erucic Acid	2	47.2	70°	1.62	38.2	1.68	39.7	Hübl	74.9	47.2
								Wijs		
Cinnamic Acid	2	107.9	75°	2.02	109.2			Hübl	16.	10.
Abietic Acid	2(?)	52.9	0°	2.0	52.8			Hanûs	33.	20.8
						—1.56	—41.2			
Rosin	?	?	0°		31.4		—47.9			
Ethyl Maleate*	2	92.9	75°	1.55	7.2	1.50	69.5			
Ethyl Fumarate*	2	92.9	20°-75°	2.00	92.6	1.18	54.4			
Ethyl Oleate*	2	51.5	25°-75°	2.34	60.4	2.27	58.4	Hanûs	83.5	52.6

* Material not purified, and probably not wholly pure.

** Results by Other Methods: Lewkowitch, Vol. I (Hübl-Wijs).
Meyer, p. 1130 (Hanûs).
Ingle, C. C. 1904 II, 506.
Johansen (Private communication).
Oleic Acid, Dunn & Hollombe-Ind. Eng. Chem. *19*, 633 (1927).

*** Ponzio (C. A. *6*, 3096 (1912)) found = Hübl 135.1, Wijs 137.3 (Iodine No.).

while still others yield entirely meaningless results unless the bromination is effected at 0°. In the case of natural mixtures or commercial products whose unsaturation cannot be calculated from formula, there is of course no way of testing the correctness of the addition-values at 0°, except by use of still lower temperature. A temperature of 0° is probably satisfactory for most substances, and many, when analyzed at 25° or higher, yield the same results as at 0°, and of course much more rapidly. 0° is probably advisable even for substances whose behavior is then not wholly normal, for the results, even though they retain a small error, should be more readily reproducible than is the case with those obtained by methods operating under the somewhat indefinite condition referred to as "room temperature."

It seems likely that the abnormal behavior attributable to excessive substitution of bromine can be further controlled by regulating the excess of bromine. A procedure for investigating this has been outlined and awaits trial.

Conclusions

(1) An aeration procedure for quantitative brominations of unsaturated substances has been developed, and found superior to the method of McIlhiney.

(2) An explanation for low or negative bromine-addition results has been discovered through use of the aeration method. By excluding operation of other causes of error, this procedure brought into prominence the spontaneous cleavage of hydrogen bromide from certain compounds when exhaustively brominated. This conclusion was verified by the experimental elimination and recovery of hydrogen bromide from such brominated compounds.

(3) The tendency of certain substances to yield abnormal saturation-values, due to the cause mentioned, has been found to be satisfactorily controllable by suitable regulation of the temperature of bromination.

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